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Structural and durability properties of hydraulic lime-pozzolan concretes

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Abstract

This paper discusses the results of a suite of tests designed to assess the structural and durability characteristics of hydraulic lime-pozzolan concretes. Specifically this paper reports on the rate of strength development, elastic modulus, linear shrinkage and rate of carbonation of four hydraulic-lime-pozzolan concretes. The purpose of this investigation was to ascertain the technical feasibility of producing high strength concretes using hydraulic lime and pozzolans as an alternative binder to Portland cement. Results have demonstrated that 28-day compressive cube strengths of 35MPa can be attained by water-cured lime-pozzolan concretes. These strengths make the material suitable for many structural applications.

The results are presented alongside comparable test results for Portland-cement (CEMI) and blastfurnace cement (CIII/A) concretes as a point of reference. Similarities and differences in material characteristics are discussed in terms of fundamental material properties and in terms of the emergent threats and opportunities for the potential development of these novel concretes.

Key words: Hydraulic lime concrete, pozzolan, compressive strength, curing, durability

Structural and durability properties of hydraulic lime-pozzolan concretes

1 Introduction

Concern about the harmful environmental impact of Portland cement (CEMI) manufacture on a global scale has prompted an extensive search for clinker replacement materials and alternative low carbon cements (LCCs) that could succeed the current technology in time. Global CEMI production exceeds 3.4×10^9 tonnes per annum [1] and is widely thought to be responsible for 5-9% of anthropogenic carbon dioxide (CO₂) emissions [2] & [3] and 2-3% of primary energy use [4]. The production of CEMI is growing at a rate of 2.5% per year [2] driven by the increasing demand for concrete, which is acknowledged to be vital for meeting the basic needs of the global construction industry.

With no other single technology promising to match the global availability and manufacturing efficiency of CEMI, a palette of prospective binder technologies are being developed [5]. Collectively these new technologies constitute a second generation of cements, which will usher in a more sustainable post-CEMI era. Amidst the development of radical new binder technologies there has been a resurgence of interest in CEMI's predecessor - lime, which, when produced at a large enough scale with the same production efficiencies as CEMI can, and in the case of some modern production facilities does [6], demand less energy and emit less CO₂ in manufacture.

A recent guide on specifying sustainable concrete in the UK has recommended that to minimise the environmental impact of concretes, best practice is to use aluminosilicate by-products, such as silica fume, fly-ash and ground granulated blastfurnace slag, in combination with Portland cement to improve aspects of performance [7]. These mineral by-products, amongst others, which are classified as Type II additions, have been shown to enhance the properties of Portland cement based concretes due to their pozzolanic or latent-hydraulic properties [8]. The utilisation of pozzolanic materials in the production of cementitious binders is far from being a new practice and long pre-dates the invention of Portland cement. Prior to the advent of Portland-cement, the cementitious properties of naturally occurring pozzolanic materials were exploited in lime-based building materials for thousands of years.

Despite a long and rich history of lime-concrete in construction, little research on the properties of hydraulic-lime concretes has been undertaken since the work of Smeaton (1724-92) and Vicat (1786-1861). The potential use of lime-concrete as an alternative to Portland cement concrete for structural components has been recognised, but it is acknowledged that 'the science has not been developed' [9]. Ten years after this knowledge gap was identified, work in this area began by considering the mechanical properties of concretes made by combining Natural Hydraulic Lime (NHL5), a building lime with a characteristic compressive strength ($f_{ck,28}$) ≥ 5 MPa and classified in accordance with BS EN 459 [10], with modern Type II additions familiar in modern concrete technology. Specifically Velosa and Cachim [11] & [12]

demonstrated that hydraulic lime-pozzolan concretes attained a mean 28-day compressive cube strength ($f_{cm,28}$) of 11 MPa with 20% of the NHL5 replaced with a waste residue of expanded clay production and a maximum $f_{cm,28}$ of 17 MPa with 20% of the NHL5 replaced with metakaolin, a calcined clay mineral.

For lime-based concretes to be a legitimate alternative to a cement-based concretes they must be capable of performing the same function, for at least as long, without any additional increase in overall binder content or total concrete volume. Although a low strength material might find some limited application a mean 28-day compressive cube strength ($f_{cm,28}$) ≥ 30 MPa, comparable with that of a low-strength cement-based concrete, is considered a minimum performance threshold. Initiated by the desire of a UK architect to build a doubly-curved shell roof for an eco-house using lime-concrete, this experimental investigation has built on the work of Velosa and Cachim [11] & [12] and focused on the strength and durability characteristics of a range of potential lime-pozzolan concretes believed to have the capability to attain compressive strengths suitable for modest structural applications.

A preliminary investigation into the strength development of hydraulic lime mortars demonstrated that it is feasible to produce high-strength lime mortars, with a comparable 28-day compressive strength to Portland cement mortars, by combining lime with alumino-silicate materials, many of which are by-products of other industrial processes. Tests conducted at a mortar scale were a precursor to the work reported herein and were aimed at identifying a small number of lime-pozzolan blends with the potential to produce a structural grade material when scaled up to lime-concretes [13].

This paper reports on the mechanical properties of four hydraulic lime-pozzolan concretes; binary and ternary combinations of a natural hydraulic lime (NHL5), silica fume (SF), metakaolin (MK), ground granulated blastfurnace slag (GGBS) and fly ash (FA).

2 Materials and methods

The experimental programme comprised the production, curing and testing of four lime-pozzolan concretes, denoted (I)-(IV). Each binder is a binary or ternary combination of natural hydraulic lime (NHL5) and alumino-siliceous mineral additions as identified from earlier work [13].

70% NHL5 with 15% FA & 15% MK (I)

50% NHL5 with 25% SF & 25% GGBS (II)

70% NHL5 with 30% SF (III)

50% NHL5 with 25% SF & 25% FA (IV)

Two reference Portland cement based concretes, a 100% Portland cement (CEM I) concrete and a 50% CEMI & 50% GGBS concrete (CIII/A), were tested concurrently

for comparison. CIII/A concretes are routinely specified in the UK and this particular CIII/A mix had 47% lower embodied CO₂ than the CEMI, based on calculations described in Mason et al (2011) [14], and thus is considered an appropriate baseline for performance in the development of alternative LCCs.

2.1 Materials

The NHL5 used was manufactured in France and supplied by a specialist lime-building merchant in the UK. The SF was obtained in the form of a slurry, with a SF:water ratio of 50:50 by mass, and conformed to BS EN 13263 [15]. The GGBS and FA conformed to BS EN 15167 [16] and BS EN 450 [17] respectively. A proprietary MK, from France, was also used. This specific product was found to be the most favourable of three alternative MKs utilised in the earlier lime-pozzolan mortar study. The CEMI used was 42,5N conforming to BS EN 197-1:2000 [18]. The major oxide composition of the materials, where this information was available from the manufacturers, is shown in Table 1.

	NHL5	SF	GGBS	FA	MK
<i>Oxide analysis (% by weight)</i>					
SiO ₂	15.0	94.5	33.0	53.0	55.0
Al ₂ O ₃	1.9	0.3	14.0	30.0	39.0
K ₂ O + Na ₂ O	0.3	1.3	0.8	0.7	1.0
Fe ₂ O ₃	0.6	0.3	0.4	7.0	1.8
TiO ₂	0.2	0.0	0.0	1.5	1.5
CaO + MgO	60.0	0.8	47.0	4.0	0.6
<i>Physical properties</i>					
BET specific surface area (m ² /kg)	800	22,000	2,650	4,090	19,000

Table 1: Properties of constituent materials

Although in the UK a water content of 175 litres/m³ is typically used to produce concrete of average consistence [19], a free water content of 240 litres/m³ was initially selected for the lime-pozzolan concretes due to the high surface area of the hydraulic lime, pozzolans and the coarse aggregate (a 10-14 mm carboniferous limestone). The particle size distribution (PSD) of the coarse aggregate was determined in accordance with BS 933-1:2012 [20] and is shown in

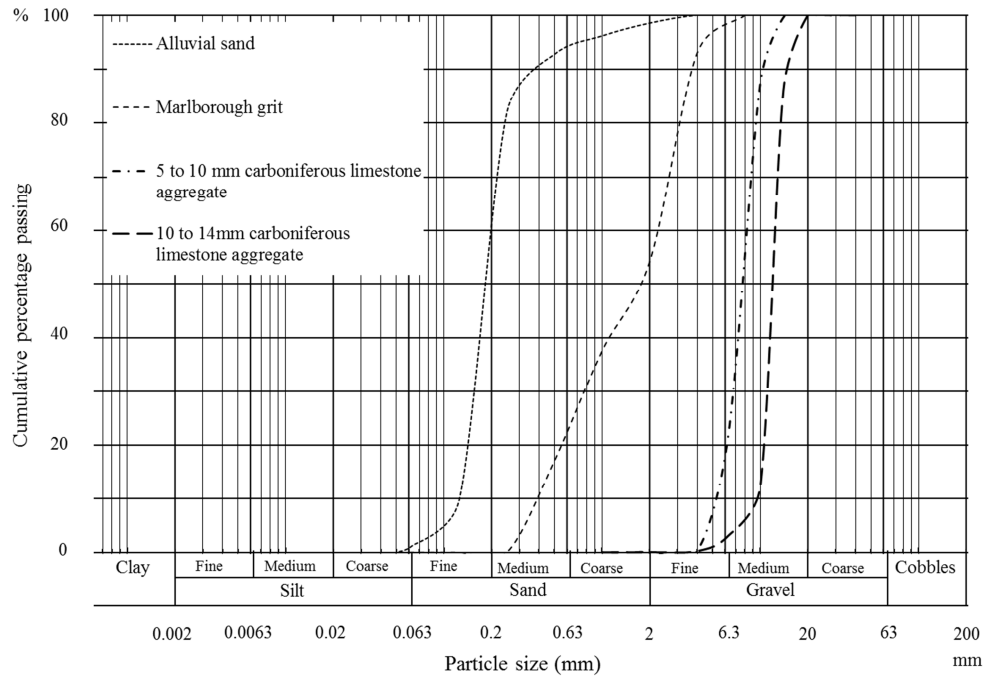


Figure 1. All the aggregates were dried under ambient conditions in the laboratory for at least 24 hours prior to use to ensure they were consistently in a lab-dry state. The coarse aggregates had an absorption coefficient of 0.6%. The total water content was corrected accordingly, to allow the aggregate to achieve a saturated surface-dry condition before mixing whilst maintaining the desired effective water content.

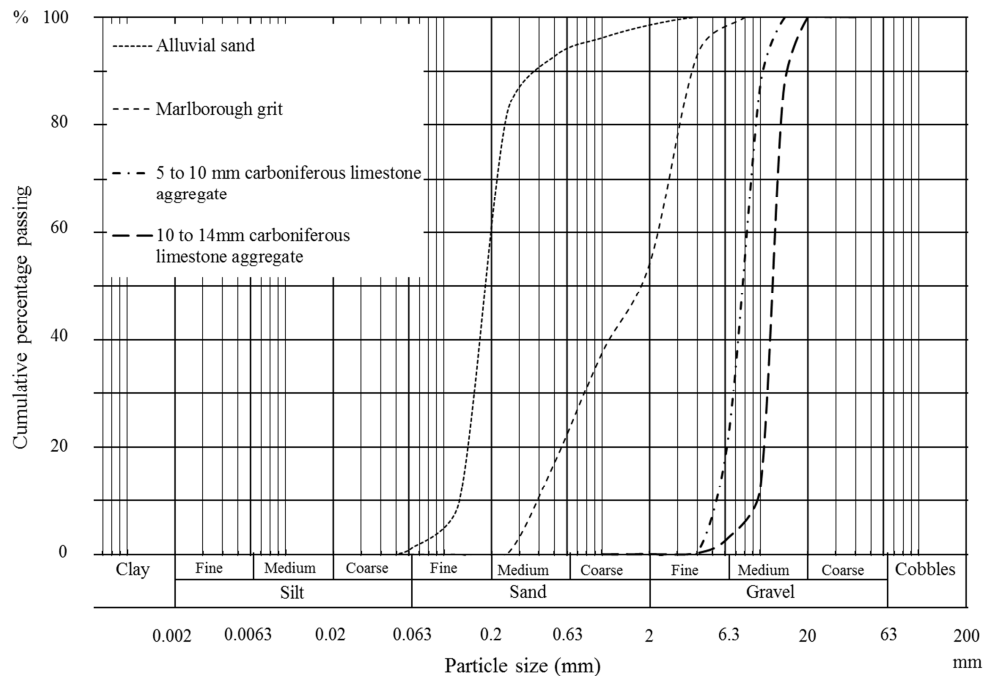


Figure 1: Particle Size Distribution [PSD] of the aggregates

The fine aggregate was 50% Marlborough grit and 50% alluvial sand by mass. The PSD of these fine aggregates was also determined in accordance with BS 933-1:2012 [20] and is also shown in

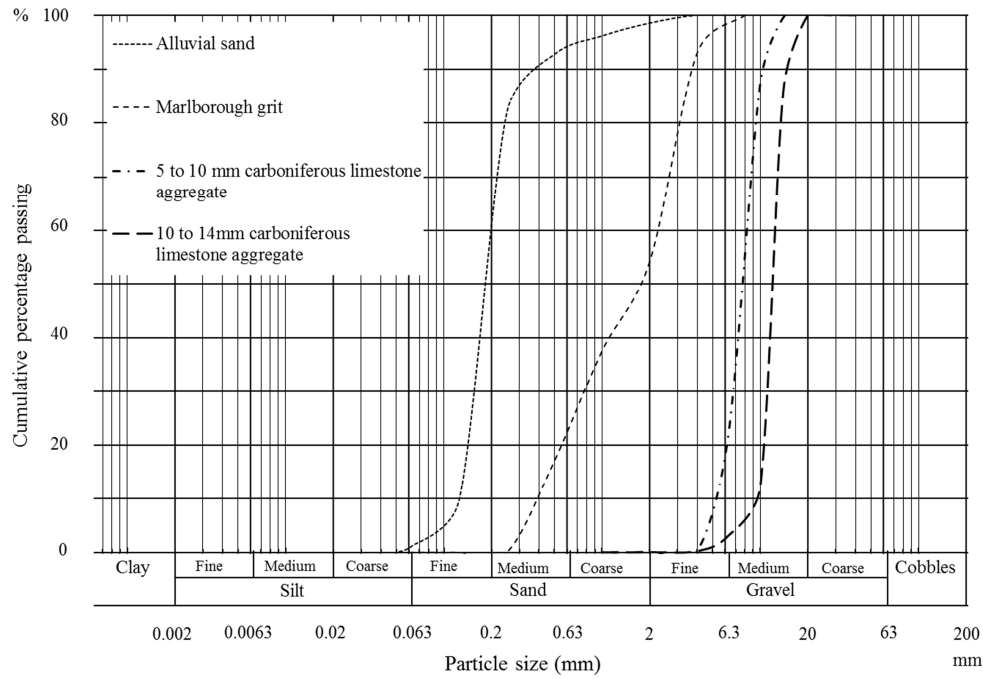


Figure 1.

2.2 Mix design

Each of the four lime-pozzolan concretes were prepared at three discrete water-to-binder (w/b) ratios in order to assess the effect of the w/b ratio on the resulting properties of the hardened material. To account for the varying densities of the alumino-silicate additions, the mass of fine sand required to maintain a consistent volumetric yield was calculated for each concrete. The Building Research Establishment's (BRE's) mix design process for concrete [21] was used as the basis for proportioning aggregates. The required volume of material for each batch was calculated based on the total volume of all the test samples plus an additional 10% for losses. Details of the mix constituents are presented in

Mixdescription	NHL5	SF	GGBS	FA	MK	PC	Total binder	Water	5-10mm	10-14mm	Alluvial sand	Marlborough grit	w/b	Density
	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³		kg/m ³
70% NHL5, 15% FA & 15% MK (I)	259	-	-	56	56	-	371	240	465	651	273	273	0.65	2272
	336	-	-	72	72	-	480	274	460	644	220	220	0.57	2298
	480	-	-	103	103	-	686	240	430	602	148	148	0.35	2253
50% NHL5, 25% SF & 25% GGBS (II)	185	93	93	-	-	-	371	240	465	651	273	273	0.79	2272
	240	120	120	-	-	-	480	316	460	644	223	223	0.65	2345
	343	171	171	-	-	-	685	378	430	602	150	150	0.55	2395
70% NHL5 & 30% SF (III)	259	111	-	-	-	-	370	240	465	651	268	268	0.65	2261
	336	144	-	-	-	-	480	266	460	644	213	213	0.55	2275
	480	206	-	-	-	-	686	240	430	602	138	138	0.35	2233
50% NHL5, 25% SF & 25% FA (IV)	185	93	-	93	-	-	371	240	465	651	263	263	0.65	2252
	240	120	-	120	-	-	480	274	460	644	205	205	0.57	2268
	343	171	-	171	-	-	685	274	430	602	128	128	0.40	2246
CEM I	-	-	-	-	-	355	355	230	405	570	178	178	0.65	1915
	-	-	-	-	-	460	460	230	400	565	230	230	0.50	2115
	-	-	-	-	-	660	660	230	380	530	295	295	0.35	2390
CEMIII/A	-	-	178	-	-	178	355	230	405	570	178	178	0.65	1915
	-	-	230	-	-	230	460	230	400	565	230	230	0.50	2115
	-	-	330	-	-	330	660	230	380	530	295	295	0.35	2390

Table 2.

Mix description	NHL5	SF	GGBS	FA	MK	PC	Total binder	Water	5-10mm	10-14mm	Alluvial sand	Marlborough grit	w/b	Density
	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³		kg/m ³
70% NHL5, 15% FA & 15% MK (I)	259	-	-	56	56	-	371	240	465	651	273	273	0.65	2272
	336	-	-	72	72	-	480	274	460	644	220	220	0.57	2298
	480	-	-	103	103	-	686	240	430	602	148	148	0.35	2253
50% NHL5, 25% SF & 25% GGBS (II)	185	93	93	-	-	-	371	240	465	651	273	273	0.79	2272
	240	120	120	-	-	-	480	316	460	644	223	223	0.65	2345
	343	171	171	-	-	-	685	378	430	602	150	150	0.55	2395
70% NHL5 & 30% SF (III)	259	111	-	-	-	-	370	240	465	651	268	268	0.65	2261
	336	144	-	-	-	-	480	266	460	644	213	213	0.55	2275
	480	206	-	-	-	-	686	240	430	602	138	138	0.35	2233
50% NHL5, 25% SF & 25% FA (IV)	185	93	-	93	-	-	371	240	465	651	263	263	0.65	2252
	240	120	-	120	-	-	480	274	460	644	205	205	0.57	2268
	343	171	-	171	-	-	685	274	430	602	128	128	0.40	2246
CEM I	-	-	-	-	-	355	355	230	405	570	178	178	0.65	1915
	-	-	-	-	-	460	460	230	400	565	230	230	0.50	2115
	-	-	-	-	-	660	660	230	380	530	295	295	0.35	2390
CEMIII/A	-	-	178	-	-	178	355	230	405	570	178	178	0.65	1915
	-	-	230	-	-	230	460	230	400	565	230	230	0.50	2115
	-	-	330	-	-	330	660	230	380	530	295	295	0.35	2390

Table 2: Mix constituents

2.3 Experimental procedures

A suite of experiments was used to assess the structural and durability characteristics of the hardened lime-pozzolan concretes. The concretes were prepared in a rotary pan mixer according to the standard procedure detailed in BS 1881-125:1986 [22] and then cast and cured in accordance with BS EN 12390-2:2009 [23]. All the specimens were covered in a sheet of polythene for 24 hours before demoulding. Curing of the concretes was in accordance with the standard procedures for each test.

2.4 Compressive strength development

To assess the influence of curing on compressive strength development, six 100mm cubes were cured in air and six in water for each concrete. Air-cured cubes were cured in a conditioning lab maintained at 20±0.5°C and 60-65% RH. Water-cured cubes were immersed in a water bath maintained at 20°C. Compressive cube strength (f_c) was measured in accordance with BS EN 12390-3:2002 [24] at 7, 28 and 56 days.

2.5 Modulus of Elasticity

The static modulus of elasticity in compression (E_c) of the concretes was determined by testing water-cured cylinders, 150mm in diameter and 300mm in height, in accordance with the method described in BS1881-121:1983 [25]. For each concrete the E_c was determined from one cylinder, following determination of the mean compressive strength (f_{cm}) of three, water-cured, 100 mm cubes from the same batch, in accordance with the standard. The testing was performed following 90 days of continuous moist curing rather than the specified 28 days.

2.6 Accelerated carbonation

The accelerated carbonation test procedure was based on a draft EN standard [26]. For each concrete, one 100x100x400 mm prism was cast and de-moulded after 24 hours. The specimens were cured in a water bath for 14 days followed by 14 days at $20\pm0.5^{\circ}\text{C}$ and 60-65% RH. After a total of 28-days curing the top, bottom and two side faces of each specimen were sealed with two coats of paraffin wax, to prevent the ingress of gaseous CO_2 . The specimens were then transferred to a chamber with active control of the temperature and concentration of atmospheric CO_2 . The temperature was maintained at 20°C and the concentration of CO_2 at 4%. The relative humidity of the chamber was maintained around 60% using a tray of saturated sodium bromide solution [27]. When analysing the results it was conservatively assumed that 1 week in the carbonation chamber was equivalent to 1 year of exposure to the atmosphere, in line with the work of others [28] & [29]. At 14 day intervals a 50 mm slice of the specimen was sampled using a bolster and chisel. The split end of the remaining specimen and any damage to the paraffin wax was then immediately resealed and the sample returned to the chamber.

The split surface of each slice was treated with a standard phenolphthalein indicator solution [30]. After one hour the depth of the carbonation front was measured using callipers. The distance between the characteristic pink stain of the indicator solution, and the outside edge of the exposed surface was read at ten discrete intervals along the edge from which an average carbonation depth was calculated.

2.7 Linear shrinkage

The linear shrinkage test was performed using a vertical comparator in accordance with ISO/DIS 1920-8 [31]. For each concrete one 75x75x280 mm prism was stored at $20\pm0.5^{\circ}\text{C}$ and 60-65% RH, the controlled conditions available, and the precise mass and length of each sample was measured and recorded at periodic intervals over a twenty week period.

3 Results and discussion

3.1 Compressive strength development

Table 3 shows the f_{cm} of water- and air-cured cubes tested at 7, 28 and 56 days. The CEMI-based reference concretes were only cured in water, but the f_{cm} of the dry-cured lime-pozzolan concretes is also presented as a percentage of the f_{cm} of equivalent wet-cured concretes.

	Age	Air-cured (20°C, 65% RH)			Water-cured (20°C, 100% RH)			Air/Water (%)		
		7	28	56	7	28	56	7	28	56
Composition	w/b									
70% NHL5, 15% FA & 15% MK (I)	0.65	4.7	6.5	6.4	6.5	9.8	11.9	71%	66%	54%
	0.57	9.6	11.2	11.4	14.0	20.5	21.7	69%	55%	52%
	0.35	10.6	12.6	12.4	17.8	23.1	24.1	60%	55%	51%
50% NHL5, 25% SF & 25% GGBS (II)	0.79	4.9	7.5	7.1	7.3	19.4	22.6	67%	38%	31%
	0.65	6.7	12.5	13.3	12.3	24.9	30.0	55%	50%	44%
	0.55	7.7	13.4	13.5	13.5	30.5	34.3	57%	44%	39%
70% NHL5 & 30% SF (III)	0.65	6.1	12.4	12.8	10.2	25.8	29.1	60%	48%	44%
	0.55	9.5	16.2	16.3	14.3	29.0	31.6	66%	56%	52%
	0.35	12.7	21.5	22.8	21.4	35.7	37.5	59%	60%	61%
50% NHL5, 25% SF & 25% FA (IV)	0.65	5.8	10.5	11.0	9.8	18.5	20.6	59%	56%	53%
	0.57	7.5	13.9	14.2	12.4	21.7	22.0	60%	64%	64%
	0.40	11.6	21.2	21.4	17.0	31.3	32.9	68%	68%	65%
CEMI	0.65	-	-	-	32.0	42.0	43.0	-	-	-
	0.50	-	-	-	36.0	46.0	54.0	-	-	-
	0.35	-	-	-	35.0	54.0	56.0	-	-	-
CEMIII/A	0.65	-	-	-	25.0	38.0	39.0	-	-	-
	0.50	-	-	-	30.0	45.0	45.0	-	-	-
	0.35	-	-	-	30.0	45.0	46.0	-	-	-

Table 3: Compressive strength development of hydraulic lime-pozzolan concretes (MPa)

The maximum $f_{cm,56}$ of the four lime-pozzolan concretes was 37.5 MPa; a strength attained by combining NHL5 (70% by mass) with SF (30% by mass) and curing the resulting concrete in water. The $f_{cm,28}$ of the equivalent air-cured concrete was 21.5 MPa, 40% lower. Three of the lime-concretes (II), (III) and (IV) attained a $f_{cm,28} \geq 30$ MPa, the minimum performance threshold identified, when cured in water but none achieved this $f_{cm,28}$ when cured in air. This suggests that hydraulic reactions govern early-age strength development in lime-pozzolan concretes and that the carbonation of free lime in the presence of atmospheric CO_2 is of lesser importance. This is a beneficial result in the development of a lime based materials for mass concrete applications.

Figure 2 shows the comparative strength development of the four lime-pozzolan concretes prepared at the same w/b ratio (w/b = 0.65). Both air- and water-cured f_{cm} results have been plotted for comparison.

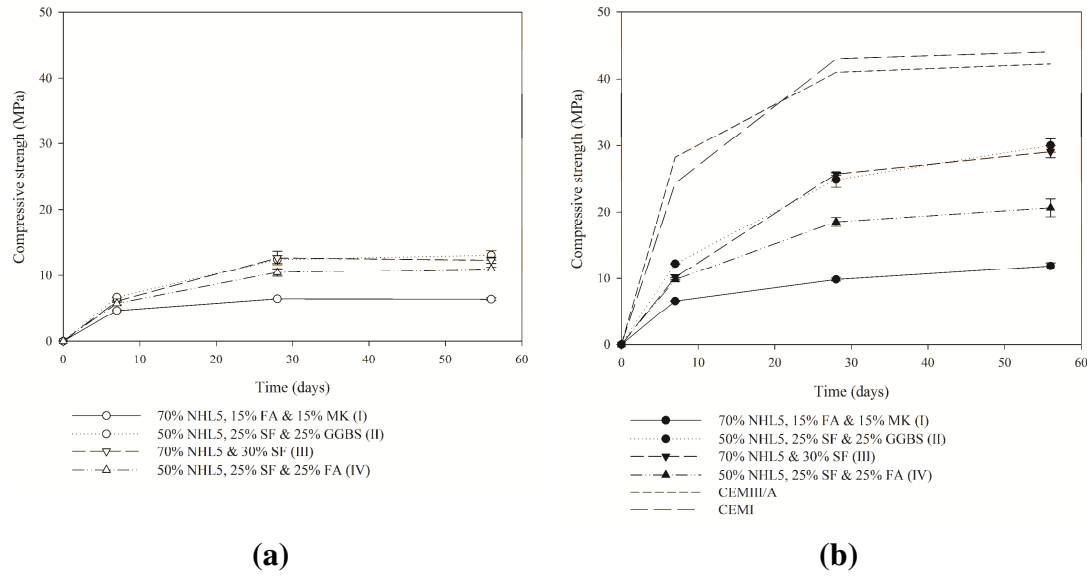


Figure 2: Strength development of (a) air- and (b) water-cured lime pozzolan concretes [$w/b = 0.65$]

The compressive strength development of the strongest two lime-pozzolan concretes was almost identical for both air- and water-cured specimens, see Figure 2 (a) & (b). The lime-pozzolan concrete with the lowest compressive strengths incorporated 15% FA & 15% MK. The order of the strength of the concretes is unaffected by the curing regime, however the two plots clearly show that curing conditions have a substantial effect on the strength development of lime-pozzolan concretes. An increased sensitivity to curing conditions might be expected as a result of the slower hydration of belite and the effect of the reaction kinetics on the resultant phase assemblage and pore structure. It is anticipated that a slower hydration reaction would be inhibited to a greater extent by the evaporation of the free-water from the capillary pores in dry-curing conditions. Certainly in CEMI concretes it has been observed that the degree of hydration of alite, cured in water for seven days and then cured in air, varied only marginally from alite cured continuously in water. Conversely, the hydration degree of the belite was substantially affected by the change in curing conditions [32].

Furthermore, the results show that the sensitivity of hydraulic lime-pozzolan concretes to sub-optimal curing conditions is affected by the inclusion of different alumino-silicate additions. At 28-days the lime-pozzolan concrete prepared with FA and MK was the least affected by dry-curing (44% reduction), whereas the lime-pozzolan concrete prepared with SF alone was most affected (52% reduction) at a w/b ratio of 0.65. The observed variation in the sensitivity of the different concretes to different curing conditions is thought to have derived from the complex interaction of chemical and physical phenomena governing the early-age reaction kinetics and structure of the hydration products. Mineral additions have for example been shown effect the evolution of capillary depression and extent of self-desiccation in CEMI-

based concretes, leading to differences in the formation of hydration products and mechanical performance [33] & [34]. Further research is needed to describe the reaction process and microstructure of lime-pozzolan concretes containing different mineral additions, with a view to explaining the macroscopic results presented in this paper.

3.2 Strength development in comparison with CEMI concretes

Having considered the effect of curing conditions on the strength gain of lime-pozzolan concretes, it is valuable to compare the cube strengths attained with those of the two reference CEMI-concretes. Figure 2 (b) shows the strength development of water-cured lime-pozzolan concretes in comparison with two water-cured reference concretes prepared at the same w/b ratio. Figure 2 (b) clearly demonstrates that the compressive strength of all four of these lime-pozzolan concretes is substantially lower than that of the CEMI-based concretes. However the difference between the strengths of these two alternative concrete-systems is shown to diminish over time. A number of interesting features can be observed from inspection of this Figure:

- The rate of strength gain between 7 and 28 days is similar for lime-pozzolan concretes (II) and (III) in comparison to the reference CEMI concretes. For these two concretes the lower $f_{cm,28}$ results can be attributed to the lower 7-day strengths ($f_{cm,7}$).
- The reduced compressive strength in lime-pozzolan concretes, in comparison to CEMI concretes, is most significant at early ages (< 7 days). This can be attributed to the low % of alite (C_3S) in the lime-pozzolan binder (0.7%) [35].
- In all four of the lime-pozzolan concretes the rate of strength gain between 28 and 56 days is greater than it is in the CEMI systems, which are observed to plateau after 28 days. This is consistent with the slower hydration of belite (C_2S) and the on-going pozzolanic reactions, which are accepted to continue after 28 days [36].

Detailed physio-chemical analysis is needed to describe the nature and progress of mechanisms by which lime-pozzolan concretes develop mechanical strength. The four chemical reactions contributing to the strength gain of these concretes are a) pozzolanic reaction of the alumina-silicates with the initial free lime (calcium hydroxide); b) hydration of the calcium silicates (primarily belite in the hydraulic lime (NHL5) but also hydraulic compounds in the GGBS) producing additional calcium hydroxide; c) pozzolanic reaction of the alumina-silicates with the calcium hydroxide produced by the hydraulic reaction and d) the carbonation of remaining free lime with atmospheric CO_2 . It is recognised that the reaction kinetics is highly complex as the rate and extent of these reactions will depend on both the constituent materials present and the curing conditions. Further investigation is necessary to investigate the reaction kinetics and the impact of constituent materials and curing

conditions on the resultant phase assemblage, pore structure and mechanical performance of lime-pozzolan concretes.

3.3 Relationship between w/b ratio and $f_{cm,28}$

The relationship between w/b ratio and $f_{cm,28}$ for the four concretes indicates the potential for producing higher strength lime-pozzolan concretes at lower w/b ratios. Figure 3 shows the relationship between w/b ratio and $f_{cm,28}$ for each of the four lime-pozzolan concretes in comparison to corresponding results for the two reference CEMI-concretes.

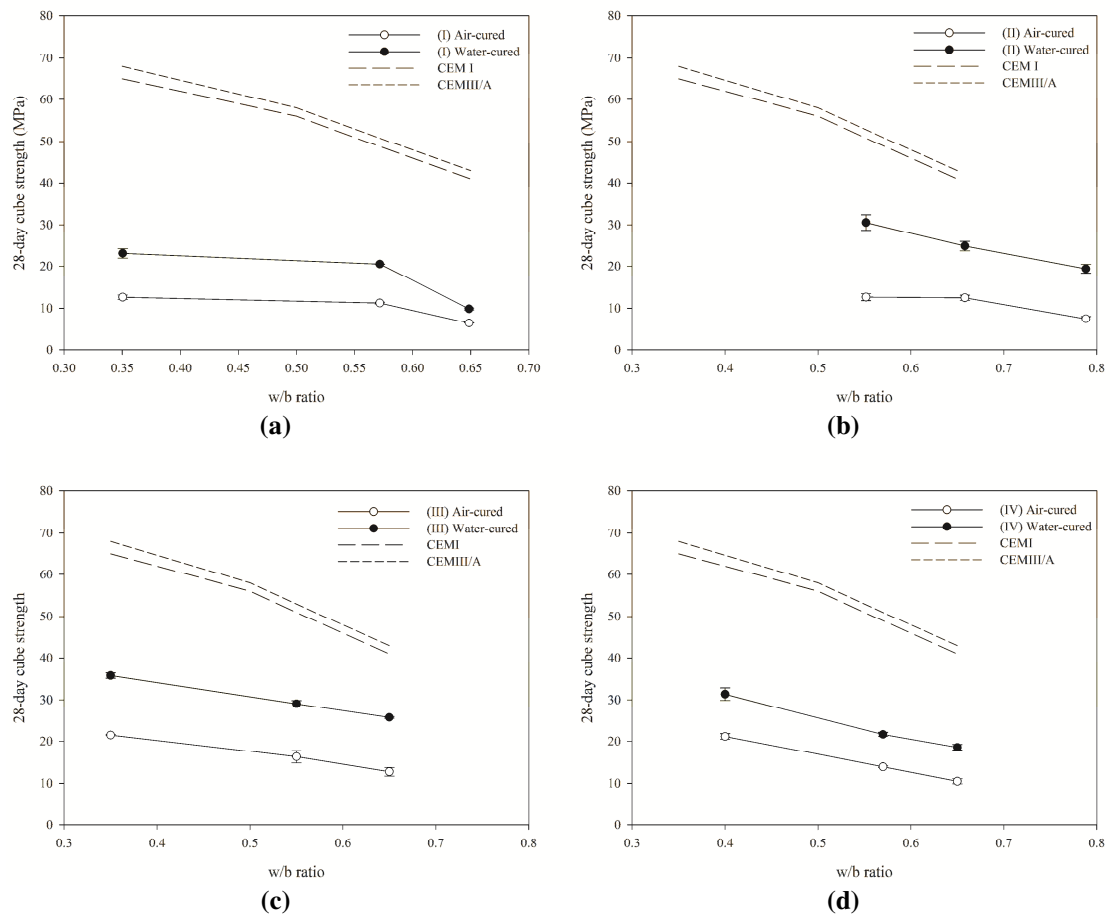


Figure 3: Relationship between w/b ratio and $f_{cm,28}$

- For fully compacted CEMI concretes compressive strength is has been shown to be related to w/b ratio as defined by Abrams law (see equation 1) [37].

$$\log(strength) = K_1 + K_2 \times \frac{W}{C} \quad (\text{equation 1})$$

Where W = the mass of free water, C = the mass of cement per unit volume and K_1 and K_2 are constants. Insufficient compaction at low w/b ratios typically prevents this idealised relationship in practice. The results plotted in Figure 3 suggest a similar relationship is true for hydraulic lime-based concretes.

- The parallel nature of air-cured and water-cured plots in each case suggest that the relationship between w/b ratio and $f_{cm,28}$ is largely unaffected by the curing conditions.
- In the case of concrete (I) the markedly reduced $f_{cm,28}$ attained by concretes prepared at a w/b ratio of 0.35, are likely to have been caused by poor compaction, leading to an increase of air voids and thus a reduction in $f_{cm,28}$ at low w/b ratios. Poor compaction in this specific case is attributed to the particularly high cohesion and poor workability of the fresh paste. This in turn can be attributed to secondary forces arising from the physical nature of the MK, which is made up of flat plate-like particles with a high-specific surface area ($19,000\text{m}^2/\text{kg}$). Although this surface area is less than that of SF ($22,000\text{m}^2/\text{kg}$), the secondary forces acting between the adjacent plates are higher than those acting between the spherical particles of SF. An attempt to improve the rheology of fresh lime-pozzolan pastes using water reducing admixtures (WRAs) revealed that this concrete was unaffected by addition of a normal low dosage of WRA. Results of this investigation are beyond the scope of this paper.
- The relationship between the w/b ratio and $f_{cm,28}$ of lime-pozzolan concretes demonstrates the potential for attaining $f_{cm,28} \geq 40\text{MPa}$ by improving compaction at w/b ratios of 0.35.

It is evident that suitable WRAs must be identified to improve compaction of lime-pozzolan binders at lower w/b ratios allowing the production of higher strength concretes. Although the observed compressive strengths of the lime-pozzolan concretes tested in this programme are significantly higher than the maximum 17 MPa reported by Velosa and Cachim [12], the strength development exhibited by the two CEMI-based reference concretes was substantially higher, particularly at early ages. The improvement in compressive strength, in comparison to the NHL5-MK concretes tested by Velosa and Cachim [12], is attributed to the use of mineral additions with a greater Pozzolanic Efficacy (PE%) [13] and production of concretes at a minimum w/b ratio of 0.35 as opposed to 0.45.

$F_{cm,28}$ results $\geq 30\text{MPa}$, attained by two of the four lime-pozzolan concretes, are thought to corroborate the technical feasibility of producing a structural strength concrete using hydraulic lime. Lime-pozzolan concretes (II) and (III), which incorporated 25% SF & 25% GGBS and 30% SF respectively, showed almost identical strength development at a w/b ratio of 0.65 and attained maximum $f_{cm,56}$ results of 37MPa and 34 MPa respectively. Analysis of the influence of w/b ratio on compressive strength of lime-pozzolan concrete (II), incorporating 25% SF & 25%

GGBS, suggests this concrete could have attained a $f_{cm,28} \geq 40\text{MPa}$ had it been possible to produce a compactable fresh concrete at a w/b ratio of 0.35.

Further physio-chemical analysis is required to explain the efficacy of the ternary combination of NHL, GGBS and SF, but these empirical test results were observed to be consistent with the findings of the preliminary study of hydraulic lime mortars [13], which evidenced a complimentary effect when pozzolans are used in ternary combinations. In this initial study of the twenty lime-pozzolan mortars; a ternary combination of 25% SF & 25% GGBS was shown to result in the greatest overall PE%, attaining a maximum $PE(\%)_{28d}$ of 94%. It is also consistent with the studies in CEMI-based concretes, which have shown a ternary combination of CEMI, SF and GGBS to be beneficial in the production of durable high-performance concretes [38].

The observation that lime pozzolan concrete (I), based on a ternary blend of NHL5, FA & MK, was consistently outperformed by the other three concretes containing SF, implies that SF, or an alternative source of soluble silica, such as rice husk ash [56], will be a key constituent of future lime-pozzolan concretes. In the preliminary lime-pozzolan mortar study [13], on which this work built, NHL5 mortars containing 15% SF and 30% SF had $PE(\%)_{28d}$ results of 78% and 92% respectively, demonstrating the favourable contribution of this mineral addition to compressive strength. Given that the dosage of SF in CEMI concretes is currently limited to a maximum of 10% [49] for both mechanical performance and for commercial viability, it is acknowledged that the high dosage of SF used in these studies may be untenable in future lime-pozzolan concretes. In recognition of commercial and legislative constraints it is recommended that future studies using SF limit its use to around 10% of the total binder

The observation that $F_{cm,28} \geq 30\text{MPa}$ was only attained by water-cured lime-pozzolan concretes is however a limitation in the potential implementation of these concretes. It is evident that appropriate curing is essential to ensure that lime-pozzolan concretes attain anticipated strengths. The observed disparity between air- and water-cured $f_{cm,28}$ suggests a considerable sensitivity to curing conditions, which must inform judicious site practice. This sensitivity is however not overly dissimilar from the sensitivity of blended CEMI concretes [39] & [40] which are routinely specified for in-situ concrete applications.

The results have highlighted that moist curing is particularly important when lime-pozzolan concretes contain a large proportion of highly reactive pozzolanic additions. This observed result is consistent with studies of blended CEMI concretes [39] & [40]. In the case of CEMI concretes a strong relationship between the total binder content and the sensitivity to curing conditions has also been shown [41]; the higher the total amount of CEMI the greater the sensitivity of the system. On this basis it is reasonable to anticipate that the sensitivity of future lime-pozzolan concretes might be

reduced by limiting the overall binder content, which at 540kg/m^3 was notably high for specified concretes.

One might note that the water- and air-cured conditions that samples are subject to in the laboratory represent extreme cases and are not representative of curing onsite. In reality site cured concrete typically comprises larger elements subject to varying conditions, including surface effects such as localised wetting and drying. The importance of concrete sensitivity to curing conditions is thus highly dependent on the project application. Greater requirements for moist curing will not favour the adoption of lime-pozzolan concretes as it tends to increase project costs by lengthening construction programmes. The sensitivity of lime-pozzolan concretes to curing conditions is expected to be reduced by the identification and use of suitable WRAs.

As with CEMI concrete, the relationship between w/b ratio and $f_{\text{cm},28}$ has a large impact on site practice, as the addition of mix water during placement has the potential to substantially reduce the concrete $f_{\text{cm},28}$. The w/b ratio of the concrete is not only affected by the addition of mix water, but also by the moisture condition of the aggregate at the point of use. For example, care must be taken when saturated aggregates are used in the production of concrete, with alterations to the mix design often necessary to prevent the additional water in the mix having an adverse effect on the strength development of the material.

A further investigation into the effect of the curing regime on the strength development of lime-pozzolan concretes demonstrated that 14 days water-curing, followed by 14 days air-curing, produced the highest $f_{\text{cm},28}$. Neville (2011) similarly shows that increased compressive strengths can be achieved by moving CEMI concrete samples from water to air after 7, 14 or 28-days [42].

3.4 Elastic modulus

The cylinder strength (f_{cyl}), elastic modulus (E_c), compressive strain at the maximum stress (ϵ_{c1}) and nominal ultimate strain (ϵ_{cu1}) for each of the four lime-pozzolan concretes are shown in Table 4.

		f_{cyl}	E_c	ϵ_{c1}	ϵ_{cu1}
Composition	w/b	MPa	GPa	%	%
70% NHL5, 15% FA & 15% MK (I)	0.65	18.4	7.0	0.003	0.003
	0.57	16.8	9.0	0.004	0.007
	0.35	22.1	21.0	0.004	0.004
50% NHL5, 25% SF & 25% GGBS (II)	0.79	19.2	7.0	0.005	0.006
	0.65	20.0	13.5	0.006	0.006
	0.55	28.1	12.5	0.004	0.006
70% NHL5 & 30% SF (III)	0.65	12.0	4.5	0.003	0.007
	0.55	19.4	8.5	0.005	0.005
	0.35	19.8	11.5	0.003	0.008
50% NHL5, 25% SF & 25% FA (IV)	0.65	15.1	14.0	0.004	0.006
	0.57	20.1	20.5	0.004	0.004
	0.40	22.3	14.0	0.003	0.003
CEMI	0.65	35.2	26.5	0.002	0.002
	0.35	62.2	28.5	0.003	0.003
CEMIII/A	0.65	40.3	22.0	0.002	0.002
	0.35	56.1	26.5	0.003	0.003

Table 4: E_c and compressive strain of lime-pozzolan concretes

The E_c of these lime-pozzolan concretes was observed to vary between 7 and 21GPa. For concrete classes $C12/15 > x \leq C50/60$ the E_c normally varies between 27-37GPa [43] and the strain at failure between 0.001 and 0.005 [42]. In the case of the four lime-pozzolan concretes the compressive strain at the maximum stress (ϵ_{c1}) is observed to vary between 0.003 and 0.006. In Eurocode 2 (EC2) the maximum compressive strain of concretes of different strength classes is provided; for concrete classes $\leq C50/60$ the highest value of ϵ_{c1} assumed for ultimate limit state design is 0.0025 [43]. All the lime-pozzolan concretes tested attained a maximum compressive strain greater than 0.0029 before failure. The results show that the nominal ultimate strain (ϵ_{cu1}) of the lime-pozzolan concretes varies between 0.003 and 0.008, the nominal ultimate strain (ϵ_{cu1}) for concrete class $\leq C50/60$ (EC2) is 0.0035 [44]. Based on these test results a reduced value of ϵ_{cu1} must therefore be assumed for design.

Figure 4 depicts the relationship between f_{cyl} and E_c of these lime-pozzolan concretes in comparison to two CEMI-based reference concretes, which are seen to correspond to the theoretical relationship defined in EC2 [43]. Consequently, from extrapolation of the results it could be suggested that lime-pozzolan concretes are less stiff than CEMI concretes of equivalent strength. The results are also compared with the empirical relationship between f_{cyl} and E_c of CEMI concretes containing pozzolanic additions, over a range of densities, as proposed by Nassif et al. (2005) [45].

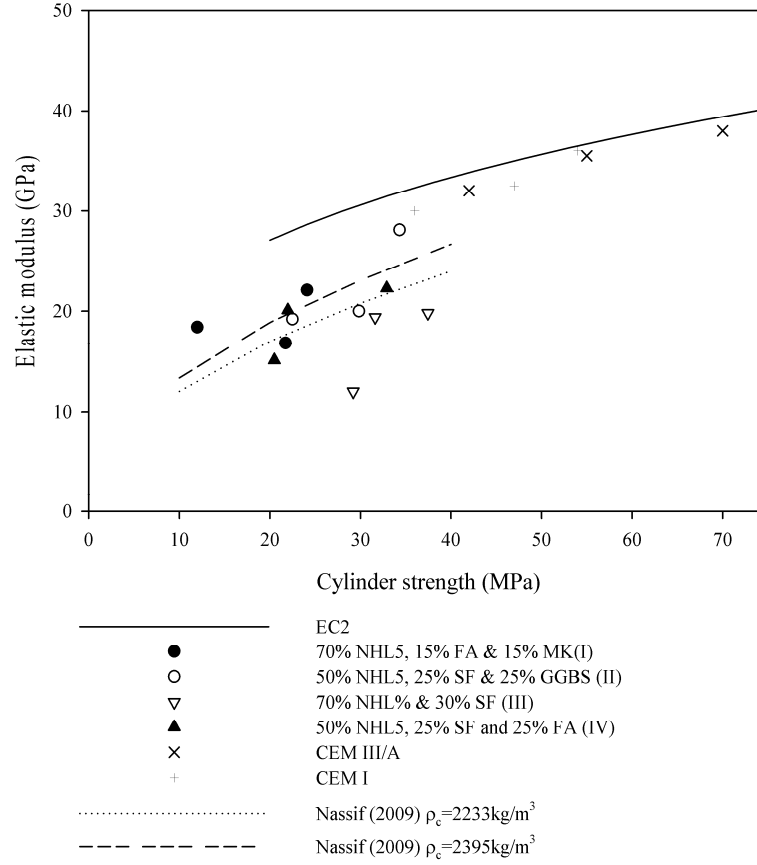


Figure 4: Relationship between E_c and f_{cyl}

The results demonstrate that the modulus of elasticity-compressive strength equation in EC2 for CEMI-concretes, substantially over-estimates the E_c of lime-pozzolan concretes. Previous studies have shown that alumina-siliceous additions have an effect on the rate of increase and maximum E_c of CEMI-based concretes [45] & [46]. Nassif et al. (2005) propose an empirical equation E_c for the high performance concrete containing pozzolanic additions, based on $f_{cyl,28}$ [45]:

$$E_c = 0.036(\rho_c)^{1.5}\sqrt{f_{cyl,28}} \quad (\text{equation 2})$$

Where ρ_c = density (kg/m^3) and $f_{cyl,28}$ = 28-day cylinder strength

Equation 2, which is plotted in Figure 5, is shown to be a reasonable predictor of the E_c of three of the four lime-pozzolan concretes tested, which had densities ranging between 2233 kg/m^3 and 2395 kg/m^3 . The lime-pozzolan concrete containing 30% SF had a lower E_c and having an average density of 2256 kg/m^3 is best described by the equation, $E_c = 0.027(\rho_c)^{1.5}\sqrt{f_{cyl}}$.

The E_c of concrete is not a determinate of structural performance at the ultimate limit state but rather the effective modulus ($E_{c,eff}$) is used to predict flexural cracking at the serviceability state [44]. The creep behaviour of lime-pozzolan concretes needs to be

established before this reduced $E_{c,eff}$ value can be deduced. With appropriate attention to serviceability criteria, the E_c of lime-pozzolan concretes is unlikely to prevent their use in the majority of structural applications. Onerous structural applications will typically be precluded by compressive strength before elastic behaviour.

3.5 Carbonation resistance

A laboratory-based test was used to determine the rate at which the carbonation front moves through the material. The results give an indication of how many years the lime-pozzolan concrete will provide protection against carbonation-induced corrosion caused by de-passivation of steel reinforcing bars. The carbonation resistance of a concrete determines the minimum amount of cover required for design in order to protect the reinforcing steel from corrosion within the lifetime of the structure.

In the assessment of concrete structures the rate of carbonation, or the CO_2 penetration rate, is assumed to obey a square root law (see eq. 2.1) [47]. The constant K_c is a property of the material and a measure of the quality of the concrete.

$$\text{carbonation depth, } x = K_c \cdot \sqrt{\text{time}} \quad (\text{equation 3})$$

Plotting the best-fit linear relationships between the average depth of the carbonation front and the square-root of the number of days in the accelerated carbonation chamber (Figure 5) clearly demonstrates that the same a square root law is valid in the behaviour of lime-pozzolan concretes.

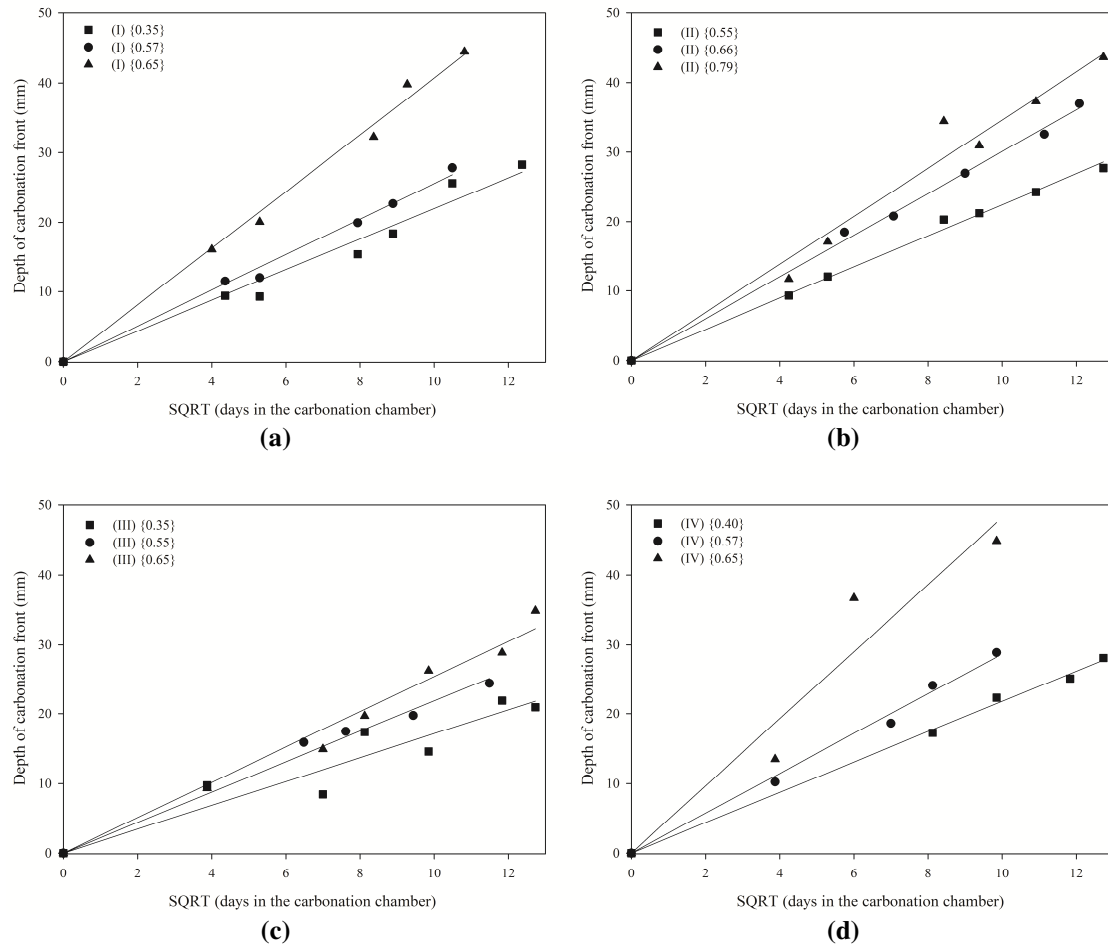


Figure 5: Measured carbonation resistance

The carbonation resistance of these lime-pozzolan concretes is lower than that of the CEMI-based concretes investigated by Dhir et al. (2001) [29]. By extrapolation of tests results presented by Dhir, a comparable CEMI concrete (with a carboniferous limestone aggregate and a water content of 240kg/m^3) at a w/b 0.65, might be expected to carbonate around 20mm in 20 weeks at 4% CO_2 exposure (where 1 week \approx 1 years natural exposure). The results in Figure 6 imply that these lime-pozzolan concretes, at a w/b ratio of 0.65, would carbonate between 30 and 60mm in the same period. This implies that lime-pozzolan concretes are less effective than CEMI concretes at protecting steel reinforcement from corrosion.

In each of four lime-pozzolan concretes it can be seen that an increase in w/b ratio increases the rate of carbonation. This is as expected, with an increased w/b ratio leading to an increased porosity and thus an easier passage of gaseous CO_2 through the hardened matrix [48]. Figure 6 shows the best-fit relationship between K_c and w/b ratio for the four lime-pozzolan concretes. The results evidence that the resistance of lime-pozzolan concretes to carbonation is proportional to the w/b ratio of the mix.

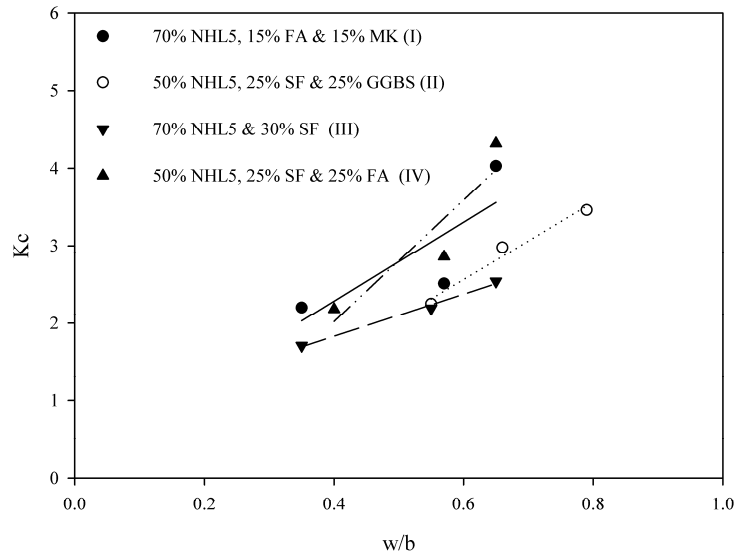


Figure 6: Relationship between w/b ratio and K_c

Not only does the inclusion of alumina-silicate additions affect the carbonation resistance of the concretes prepared at a given w/b ratio, but the varying gradients of the best-fit linear relationship between K_c and w/b ratio (shown in Figure 6) suggests a variation in the sensitivity of the four lime-pozzolan concretes to changes in w/b ratio. The carbonation resistance of the lime-pozzolan concrete prepared with 30% SF is least affected by the variation in w/b ratio at which it is prepared, whereas lime-pozzolan concrete prepared with 25% SF and 25% FA is observed to be the most sensitive. Given that carbonation resistance is highly dependent on the pore structure of the matrix, the sensitivity of the different lime-pozzolan concretes to changes in w/b will be affected by the reactivity and phase assemblage of the alumino-silicates [49].

Composition	w/b	K_c	Theoretical years to carbonate 40 mm	Theoretical years to carbonate 50 mm
70% NHL5, 15% FA & 15% MK (I)	0.65	3.6	18	28
	0.57	2.8	29	46
	0.35	2.0	56	87
50% NHL5, 25% SF & 25% GGBS (II)	0.79	2.8	29	45
	0.65	2.1	54	84
	0.55	1.3	133	207
70% NHL5 & 30% SF (III)	0.65	2.5	36	57
	0.55	2.1	52	81
	0.35	1.7	80	124
50% NHL5, 25% SF & 25% FA (IV)	0.65	4.0	14	23
	0.57	2.8	29	45
	0.40	1.6	86	135

Table 5: Rate of carbonation

Table 5 provides calculated K_c values for each of the lime-pozzolan concretes prepared at standard w/b ratios based on extrapolated results.

Although the carbonation resistance of lime-pozzolan concretes is low in comparison to CEMI concretes it can be suggested from the results that a lime-pozzolan concrete incorporating 25% SF & 25% GGBS may be able to provide sufficient protection for steel reinforcement for around 130 years. Increasing the depth of cover from 40 to 50 mm increases this to over 200 years. A previous study looking at the carbonation resistance of blended CEMI concretes, has shown that a ternary binder incorporating both SF and GGBS is highly effective in producing a dense pore structure, which hampers the diffusion of CO_2 [30].

Extrapolation of the results suggests that, at a w/b ratio of 0.35, three of the four lime-pozzolan concretes, (II), (III) & (IV) could provide in excess of 60 years protection from 40mm cover. This observed result reinforces the need to identify a suitable WRA to facilitate production of lime-pozzolan concretes at low w/b ratios.

Although lime-pozzolan concretes have been shown to provide adequate carbonation-resistance to provide sufficient protection for carbon steel for the typical design life of a modern building, the durability of ancient lime-pozzolan concrete structures, raises a question about the appropriateness of this composite structural solution. If passivation of carbon steel is a critical requirement of this new concrete technology then it might be appropriate to terminate this line of inquiry, on the basis of the observed results, even at this early stage. However if non-metallic reinforcement bars or fibres are to be increasingly utilised, removing this particular durability requirement, then the rate of carbonation might rather be conceptualised as the carbon-dioxide capture rate. In this scenario the increased rate at which this material absorbs atmospheric CO_2 might be deemed beneficial and could potentially be used as a mechanism for sequestering atmospheric CO_2 and offsetting CO_2 emissions associated with the manufacture of the binder.

Alternative reinforcement options include both non-metallic reinforcement bars, such as glass or basalt fibre reinforced polymers [50] or bamboo [51] as well as Fibre Reinforced Concrete (FRC) solutions containing dispersed synthetic or natural fibres such as sisal, hemp and coir [52] & [53]. Stainless or galvanised steel reinforcement could feasibly be used in lime-pozzolan concretes, but the typical cost of these solutions would generally be prohibitive and their use likely to negate environmental benefits associated with specifying the lime-pozzolan concrete. Cathodic protection is another potential solution for carbon-steel reinforced lime-pozzolan concrete structures exposed to the environment.

3.6 Linear shrinkage

This test determines the rate and extent to which a sample of lime-pozzolan concrete will shrink during curing at standard conditions.

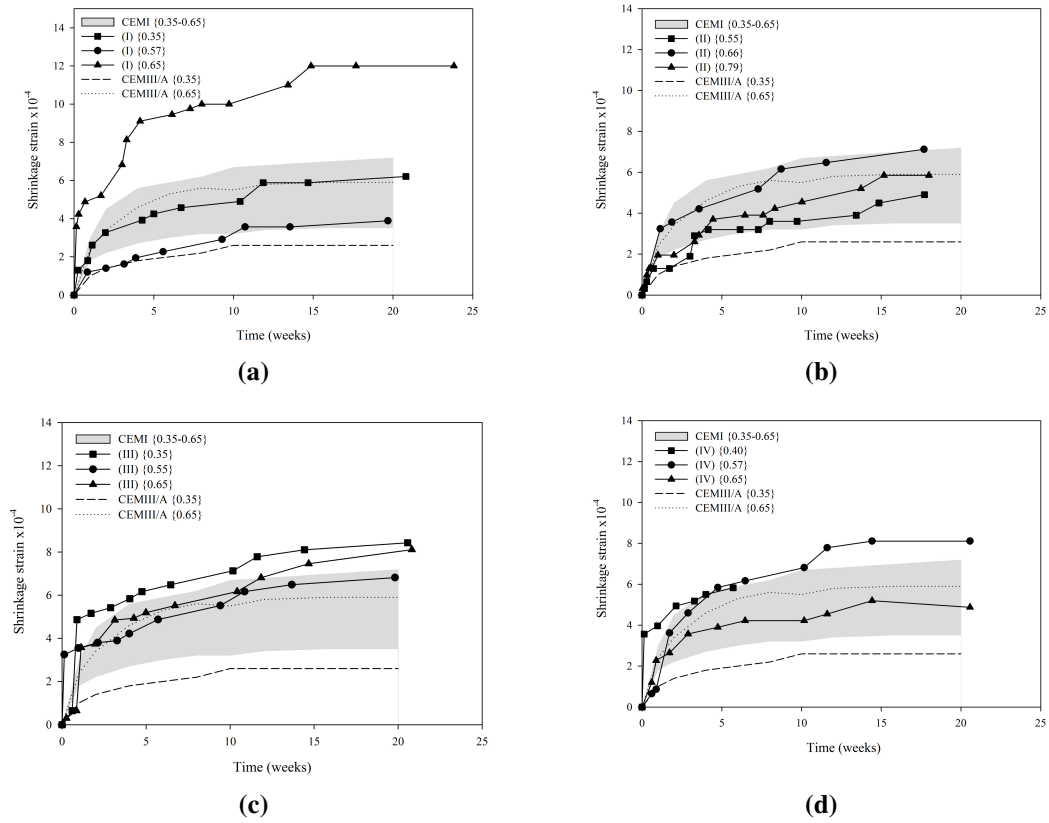
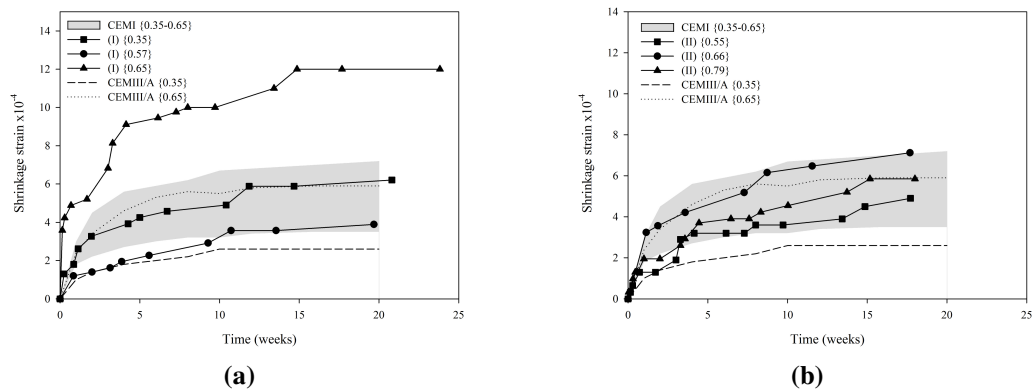


Figure 7 shows the change in the calculated shrinkage strain over time in comparison to equivalent measurements on reference CEMI and CIII/A concretes.



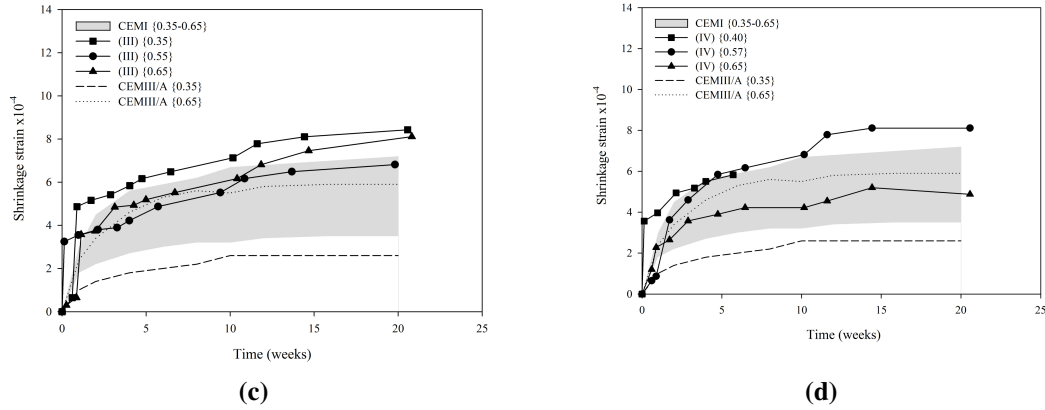


Figure 7: Linear shrinkage of lime-pozzolan concretes

Although the results show that the w/b ratio of the concrete clearly affects the total linear shrinkage of the specimen, no clear relationship between the two properties is seen in the results. Typically a higher w/b ratio would be expected to result in a higher shrinkage strain, due to the increased potential for volumetric changes resulting from the evaporation of the free water during drying. However for samples prepared at low w/b ratios, the measured shrinkage could have been affected by on-going autogenous shrinkage, which in the case of CEMI-concrete is assumed to have been completed in the initial period of water curing. It has previously been shown that SF has a substantial impact on the autogenous shrinkage of high-strength CEMI concretes, with 15% of SF increasing autogenous shrinkage by 50% [54]. A slower hydration reaction leading to longer-term self-desiccation in lime-pozzolan concretes could, for example, have resulted in the in concrete (III) exhibiting the maximum linear shrinkage at the minimum w/b ratio [0.35].

Figure 7 graph (II) clearly shows that the linear shrinkage of a lime-pozzolan concrete incorporating 25% SF and 25% GGBS is within the range of shrinkage measurements for the CEM 1 reference concrete [0.35-0.65] at all w/b ratios. The linear shrinkage of the lime-pozzolan containing 30% SF (III) was observed to be greater than that of the CEMI reference concretes but this was the concrete whose shrinkage was least affected by the variation of the w/b ratio at which it was prepared. In contrast lime-pozzolan concrete (I), the only concrete not containing any SF, displayed a very broad range of shrinkage strain values. Although the shrinkage of this lime-pozzolan concrete was comparable with the CEMI concrete at a w/b ratio of 0.35, the shrinkage strain was observed to be almost twice that of the CEMI concrete when compared at a w/b ratio of 0.65. These observed results not only highlight the considerable sensitivity of lime-pozzolan concrete (IV) to changes in w/b ratio but also make a case for the inclusion of SF for limiting the sensitivity of lime-pozzolan concretes to shrinkage in applications where this is important.

Comparing the results of the two reference concretes it is apparent that inclusion of 50% GGBS is effective in reducing the linear shrinkage of CEMI-based concretes.

Similarly the least drying shrinkage, across all w/b ratios, was seen observed in lime-pozzolan concrete (II), incorporating 25% SF and 25% GGBS.

Further physio-chemical analysis is needed to explain the large dispersion of the linear shrinkage results, thought to derive from the rate, extent and nature of the reaction products in the case of each lime-pozzolan binder. This analysis was beyond the scope of this research, which was concerned with the structural properties of lime-pozzolan concretes as indicator of their potential structural application. Relative differences in the linear shrinkage of the different lime-pozzolan concretes are discussed, with reference to the performance of comparable CEMI concretes, so as to comment on the appropriateness of alternative lime-pozzolan binders in future structural applications.

The importance of limiting the ultimate drying-shrinkage of concretes is highly dependent on their application in use. It is the restraint provided by support conditions, or friction at the interface of discrete materials, which tends to constrain deformation and induce cracking or warping of concrete elements during drying. Limiting drying shrinkage is particularly crucial in the case of ground floor slabs where drying shrinkage can lead to curling of slabs as well as detrimental cracking. In many applications it is important to know the maximum shrinkage strain for design, for example in the case of pre-stressed concrete, where drying shrinkage acts to reduce pre-stressing forces.

The observed drying shrinkage of the tested lime-concrete specimens was, in the vast majority of cases, broadly in line with that of the CEMI-based control concretes over a 20 week period. The ultimate strains of all the concretes tested, including the controls, were shown to be slightly higher than the ultimate strain of 560 microstrain, calculated, in accordance with CIRIA Guide C660 [55], for an equivalent Class N CEMI concrete stored at 20°C and 60-65%.

Given the shrinkage strain plot for the lime-pozzolan concretes does not clearly plateau within the first 20-weeks of testing, it is clear that drying shrinkage needs to be monitored over a longer period before an ultimate shrinkage strain can be defined for design purposes. In practise incorrect detailing of lime-pozzolan concretes could lead to cracking or deformation over a longer period. However provided that the ultimate shrinkage strain is not found to be substantially higher than the 20-week results imply, it would be feasible to accommodate this degree of drying shrinkage in design.

That said, the results also suggest that there are opportunities to minimise the drying shrinkage of lime-pozzolan concretes through the selection and combination of alumino-siliceous additions. The results suggest for example that SF is effective in minimising the sensitivity of lime-pozzolan concretes to variations in w/b ratio. This is clearly beneficial in practise as it mitigates the risk of high w/b ratios leading to

excessive shrinkage. The results of the control samples also suggest that the incorporation of 50% GGBS is effective in reducing the linear shrinkage of CEMI-concretes. Similarly the high proportion of GGBS in concrete (II) could have been responsible for limiting shrinkage in comparison to concrete (III). The sensitivity of concrete (I) to changes in w/b ratio raises concerns about the suitability of this ternary combination of additions.

From a technological perspective observed similarities in the mechanical behaviour and performance of lime-pozzolan and CEMI concretes engender confidence in this novel concrete technology, whilst differences provide opportunities for developing lime-pozzolan concretes with beneficial properties which would differentiate this future material from the current technology. Superior performance need not necessarily demand greater mechanical strengths. Rather enhanced performance might be manifested in improved compatibility with other construction materials, or systems, or differential properties such as breathability, flexibility or the absorption of CO₂. Additional structural characteristics that will be of interest in the development of lime-pozzolan concrete include tensile strength and creep.

With no single cementitious binder promising to match the wide scale availability and universal applicability of CEMI, we might be headed towards a diversification of the concrete market, with a palette of new low CO₂ binders appropriate to specific applications and geographical locations. This ‘engineered’ concrete model underpins high-performance concrete (HPC) technology [44], although this terminology increasingly tends to refer to particularly high-strength concretes.

4 Conclusions

The purpose of this investigation was to ascertain the technical feasibility of producing a structural strength concrete using hydraulic lime as an alternative cementitious binder to CEMI. $F_{cm,28}$ results ≥ 30 MPa, attained by two of the four lime-pozzolan concretes reported in this paper, are thought to corroborate the technical feasibility of producing a structural strength concrete using hydraulic lime.

The maximum $f_{cm,28}$ of the four lime-pozzolan concretes was 35.7 MPa; a strength attained by combining NHL5 (70% by mass) with SF (30% by mass) and curing the resulting concrete in water. The $f_{cm,28}$ of the equivalent air-cured concrete was 21.5 MPa, 40% lower. The sensitivity of hydraulic lime-pozzolan concretes to sub-optimal curing conditions was observed to be affected by the inclusion of different aluminosilicate additions.

Lower $f_{cm,28}$ results in comparison to reference CEMI concretes, were seen to derive from lower 7-day strengths, with otherwise a similar strength gain between 7 and 28 days. The fact that the rate of strength gain between 28 and 56 days was greater in all

four of the lime-pozzolan concretes than it was in the CEMI systems, suggests further work is needed to investigate the long term strength of lime-pozzolan concretes.

Lime-pozzolan concretes have been seen to be less stiff than CEMI concretes of equivalent strength, with the E_c of the lime-pozzolan concretes tested observed to vary between 7 and 21GPa.

The carbonation resistance of lime-pozzolan concretes has been observed to be low in comparison to CEMI concretes, across all w/b ratios. Lime-pozzolan concrete (II), incorporating 25% SF & 25% GGBS, has a carbonation coefficient (K_c) of 1.3-2.8, suggesting that 40mm of cover would provide sufficient protection for steel reinforcement for around 130 years. In each of four lime-pozzolan concretes it can be seen that an increase in w/b ratio increases the rate of carbonation.

The observed drying shrinkage of the tested lime-concrete specimens was, in the vast majority of cases, broadly in line with that of the CEMI-based control concretes over a 20 week period. However, the degree of shrinkage was observed to be influenced by both the w/b ratio and constituent materials. The least drying shrinkage was seen observed in lime-pozzolan concrete (II), incorporating 25% SF and 25% GGBS, which was within the range of shrinkage measurements for the CEMI reference concrete [0.35-0.65] at all w/b ratios. With respect to shrinkage, SF was observed to limit the sensitivity of the lime-pozzolan concretes to changes in w/b ratio. The broad range of shrinkage strain values observed in the case lime-pozzolan concrete (I), the only lime-concrete not containing SF, questions the suitability of this ternary combination of additions in structural applications.

Across all the tests it was seen that the production of lime-pozzolan concretes at low w/b ratios results in the strongest and most durable concretes. Subsequent testing will focus on the development of a ternary blend of NHL5, SF and GGBS, which of the four lime-concretes tested showed the best potential for a high-strength structural grade lime-concrete. Lime-pozzolan concrete (II), incorporating 25% SF and 25% GGBS, exhibited the greatest initial and long term strength gain, the highest strain at the maximum compressive strength, the greatest carbonation resistance and the least drying shrinkage.

Where it has been possible to provide the results of comparative testing on equivalent CEMI-concretes, it has been seen that the lime-pozzolan concretes tested, exhibited only moderate strengths and tolerable durability in comparison with the reference CEMI-concretes. With the global cement industry exploiting considerable economies of scale in the supply of low cost CEMI into the market, it seems that only superior performance, in conjunction with reduced environmental impact, will see innovative cements becoming a viable alternative.

References

- [1] CEMBUREAU ACTIVITY REPORT 2011. Brussels: The European Cement Association, 2012.
- [2] Metz B. Mitigation of Climate Change: Working Group III Contribution to the Fourth Assessment Report of the IPCC. Cambridge: Cambridge University Press, 2007.
- [3] Harrison AJW. Low carbon cements and concrete in modern construction. In: UKIERI Concrete Congress - Innovations in Concrete Construction. Jalandhar: 2013. p.723-46.
- [4] Juenger MCG, Winnefeld F, Provis JL. Advances in alternative cementitious binders. *Cem Concr Res* 2011;41(12):1232-43.
- [5] Shi C, Jiménez AF, Palomo A. New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cem Concr Res* 2011;(4):750-63
- [6] Chaux & Enduits de Saint Astier. CO₂ emissions of various binders: St. Astier Natural Hydraulic Limes (NHL). <<http://www.stastier.co.uk/nhl/testres/co2emissions.htm>> [updated 2006, accessed 2012].
- [7] Mineral Products Association. Specifying Sustainable Concrete. London: The Concrete Centre, 2011.
- [8] Bye GC. Portland Cement, Third Edition. London: ICE Publishing, 2011.
- [9] Holmes S, Wingate M. Building with Lime - A practical introduction. Rugby: Practical Action Publishing, 1997
- [10] British Standards Institute. BS EN 459-1 Building Lime - Definitions, specifications and conformity criteria. London: BSI, 2010.
- [11] Velosa AL, Cachim PB. Hydraulic-lime based concrete: Strength development using a pozzolanic addition and different curing conditions. *Constr Build Mater* 2009;23(5):2107-11.
- [12] Cachim P, Velosa AL, Rocha F. Effect of Portuguese metakaolin on hydraulic lime concrete using different curing conditions. *Constr Build Mater* 2010;24(1):71-78.
- [13] Grist E, Paine KA, Heath A, Norman J. Compressive strength of binary and ternary lime-pozzolan mortars. *Mater Des* 2013;(52):514-23.
- [14] Paine KA, Mason J, Rogers K. Low carbon concrete: Guidelines for reducing the carbon footprint of concrete used in flood risk management infrastructure - Black and Veatch Report to the Environment Agency. London: Black and Veatch, 2011.
- [15] British Standards Institute. BS EN 13263-1 Silica fume for concrete: Definitions, requirements and conformity criteria. London: BSI, 2005.
- [16] British Standards Institute. BS EN 15167-1 Ground granulated blast furnace slag for use in concrete, mortar and grout —Part 1: Definitions, specifications and conformity criteria. London: BSI, 2006.
- [17] British Standards Institute. BS EN 450-1 Fly ash for concrete: Definition, specifications and conformity criteria. London: BSI, 2012.
- [18] British Standards Institute. BS EN 197-1 Cement Part 1: Composition, specifications and conformity criteria for common cements. London: BSI, 2011.
- [19] Dhir R, Hewlett P. Cement: a question of responsible use. *Concr* 2008;42(7):40-42.
- [20] British Standards Institute. BS 933-1 Tests for geometrical properties of aggregates: Determination of particle size distribution — Sieving method. London: BSI, 2012.
- [21] Teychenné DC, Franklin RE, Erntroy HC, Marsh BK. Design of normal concrete mixes: 2nd Edition. Watford: Building Research Establishment, 1997.

- [22] British Standards Institute. BS EN 1881-125 Testing concrete - methods for mixing and sampling fresh concrete in the laboratory. London: BSI, 1986.
- [23] British Standards Institute. BS 12390-2 Testing hardened concrete - Making and curing specimens for strength tests. London: BSI, 2009.
- [24] British Standards Institute. BS 12390-3 Testing hardened concrete - compressive strength test of specimens. London: BSI, 2009.
- [25] British Standards Institute. BS EN 1881-121 Testing concrete: Method for determination of static modulus of elasticity in compression. London: BSI, 1983.
- [26] British Standards Institute. DD CENTS 12390-10 Testing hardened concrete - determination of the relative carbonation resistance of concrete. London: BSI, 2007.
- [27] Greenspan L. Humidity fixed points of binary saturated aqueous solutions. J Res Natl Bur Stand 1977;81(1):89-96.
- [28] Ho DWS, Lewis RK. Carbonation of concrete and its prediction. Cem Concr Res 1987;17(3):489-504.
- [29] Dhir R, Paj T, MJ, M. Role of cement content in the specification for durability of concrete. Dundee: University of Dundee Concrete Technology Unit, 2001.
- [30] Sulapha P, Wong SF, Wee TH, Swaddiwudhipong S. Carbonation of concrete containing mineral admixtures. J Mater Civ Eng 2003;15(2):134-43.
- [31] British Standards Institute. BS ISO 1929-8 Testing of concrete: Determination of drying shrinkage of concrete. London: BSI, 2009.
- [32] Termkhajornkit P, Nawa T, Kurumisawa K. Effect of water curing conditions on the hydration degree and compressive strengths of fly ash–cement paste. Cem Concr Compos 2006;28(9):781-89.
- [33] Persson B. Seven-Year Study on the Effect of Silica Fume in Concrete. Adv Cem Based Mater 1998;7(3):139-155
- [34] Darquennes A, Khokhar MIA, Rozière E, Loukili A, Grondin F, Staquet S. Early age deformations of concrete with high content of mineral additions. Constr Build Mater 2011;25:1836-47
- [35] Chaux & Enduits de Saint Astier. Mineralogy and Chemistry of Raw Materials and Products. <<http://www.stastier.co.uk/nhl/testres/minchem.htm>> [updated 2006, accessed 2012].
- [36] Massazza F. Pozzolanic Cements. Cem Concr Compos 1993;15:185-214
- [37] Sear LKA, Dews J, Kite B, Harris FC, Troy JF. Abrams law, air and high water-to-cement ratios. Constr Build Mater 1996;10(3):221-226
- [38] Bagheri AR, Zanganeh H, Moalemi MM. Mechanical and durability properties of ternary concretes containing silica fume and low reactivity blast furnace slag. Cem Concr Compos 2012;34(1):663-670
- [39] Ramezaniapour AA, Malhotra VM. Effect of curing on the compressive strength, resistance to chloride-ion penetration and porosity of concretes incorporating slag, fly ash or silica fume. Cem Concr Compos 1995;17(2):125-33.
- [40] Ozer B, Ozkul MH. The influence of initial water curing on the strength development of ordinary portland and pozzolanic cement concretes. Cem Concr Res 2004;34(1):13-18.
- [41] Atiş CD, Özcan F, Kılıç A, Karahan O, Bilim C, Severcan MH. Influence of dry and wet curing conditions on compressive strength of silica fume concrete. Build Environ 2005;40(12):1678-83.

- [42] Neville AM. Properties of Concrete. London: Prentice Hall, 2011.
- [43] British Standards Institute. BS EN 1992-1-1 Eurocode 2: Design of concrete structures. London: BSI, 2004.
- [44] Mosley B, Bungey J, Hulse R. Reinforced concrete design to Eurocode 2. Basingstoke: Palgrave Macmillan, 2007.
- [45] Nassif HH, Najm H, Suksawang N. Effect of pozzolanic materials and curing methods on the elastic modulus of HPC. *Cem Concr Compos* 2005;27(6):661-70.
- [46] Mazloom M, Ramezaniapour AA, Brooks JJ. Effect of silica fume on mechanical properties of high-strength concrete. *Cem Concr Compos* 2004;26(4):347-57.
- [47] The Concrete Society. Diagnosis of deterioration in concrete structures. Camberley: The Concr Soc, 2000.
- [48] Price WH. Factors influencing concrete strength. *ACI J Proc* 1951;47(2): 417-32
- [49] Cultrone G, Sebastian E, Huertas MO. Forced and natural carbonation of lime-based mortars with and without additives: Mineralogical and textural changes. *Cem Concr Res* 2005;35(12):2278-89.
- [50] Lopresto V, Leone C, De Iorio I. Mechanical characterisation of basalt fibre reinforced plastic. *Compos Part B: Eng* 2011;42(4):717-23.
- [51] Ghavami K. Ultimate load behaviour of bamboo-reinforced lightweight concrete beams. *Cem Concr Compos* 1995;17(4):281-88.
- [52] Coutts RSP. A review of Australian research into natural fibre cement composites. *Cem Concr Compos* 2005;27(5):518-26.
- [53] Brandt AM. Fibre reinforced cement-based (FRC) composites after over 40 years of development in building and civil engineering. *Compos Struc* 2008;86(1):3-9.
- [54] Mazloom M, Ramezaniapour AA, Brooks JJ. Effect of silica fume on mechanical properties of high-strength concrete. *Cem Concr Compos* 2004;26(4):347-57.
- [55] Bamforth PB. Early-age thermal crack control in concrete C660. London: CIRIA, 2007.
- [56] Henry M, Kato Y. The role of new material technologies for sustainable practice in the concrete industry. In: Portland International Conference on Management of Engineering & Technology. PICMET: 2009. pp. 1738-44.

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